

DOES THE GLASS ELECTRODE DETERMINE THE SAME pH-VALUES ON THE SKIN SURFACE AS THE QUINHYDRONE ELECTRODE?*

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The first investigations dealing with the degree of acidity on the skin surface were made by way of colorimetry (Hess, Sharlitt and Scherr). The measuring accuracy, however, was very poor and hence this procedure was not generally accepted as a satisfactory method. The electrometrical measuring technic for the pH-determination on the skin surface by Marchionini and Schade (9-14) thus was the first essential improvement in this field, and since then all experiences in electrometering were made with quinhydrone electrodes.

Since the glass electrode has been employed for the determination of pH on the skin we took great interest in determining whether the pH-values found by the glass electrode could be easily compared with those found by the quinhydrone electrode—and all the more so as the two electrode systems determine pH-values by means of two basically different principles.

There are various reasons to account for the fact that glass electrodes—contrary to quinhydrone electrodes—were so reluctantly employed in the pH-determination of the skin. First of all, glass electrode measuring demands a greater complexity of mechanical devices; and furthermore is—as compared with quinhydrone electrodes—far more easily affected by interfering influences due to environment and to the technic of the individual taking the measurements. In contrast to the quinhydrone electrode that first was introduced in skin surface measuring by Marchionini and Schade, it demands (being a high-resistant glass electrode) a valve voltmeter that is far more expensive than the simple compensator. But the main difficulty in employing the glass electrode for surface measuring is the construction of the glass electrode foot, that has to vary from the standard ball type form generally employed for diving measuring chains as it has to conform to the skin with the help of a plane membrane surface. In 1942 Klefehn (4) reported on trying unsuccessful glass electrode investigations aimed at the pH-determination on surfaces. Although it was possible to flatten the sparkling ball these “flat electrodes” proved very fragile and inclined to break from the very beginning, so that eventually they could not be employed for further measurements and the investigations were finally dropped altogether.

It was, for the first time, in 1939 that Blank (2) in the United States succeeded in taking pH-measurements on the skin surface with a glass electrode. But it was not until a short time ago that information on further pH-measurements with glass electrodes appeared in publication.

The applicability of the glass electrode for the general pH-determination is, according to Kratz (8), based on the process of the formation of phase limit

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Received for publication August 6, 1953.

potential between the glass membrane and the electrolytic solutions which, with adequate glass types, depends nearly exclusively on the hydrogen ion concentration of the solution as the glass membrane acts like a diaphragm that is permeable for H-ions only.

The potential of the quinhydrone electrode chain, however, first of all represents an oxidation-reduction-potential with which the ratio of quinone to hydroquinone in the suspension of the acids, ampholytes, and salts in the upper layer of the skin is decisive for the quantity of the potential to be measured. Hence, numerous authors objected to the reliability of quinhydrone electrode measurements since these possibly are subject to heavy interfering influences by the redox systems on the skin.

For taking comparative pH-measurements on the skin with two different electrode chain systems, one modern flat glass electrode for surface measurements (Ingold) (3) and one quinhydrone electrode for skin measurements (after Kordatzki and Schirren) (6-7, 15) were available. As the glass electrode had a plane membrane, its entire surface could be easily placed in contact with the skin area to be measured. This was an essential premise for measurements that were to be reproduced. All in all, the flat glass electrode employed corresponded to the design suggested by MacInnes and Dole for pH-measurements in the hanging drop. The stability of the plane measuring membrane was so that the glass electrode could be put directly on the moist skin surface without running the risk of breaking it. In both cases calomel electrodes were used. The groundings were likewise screened and isolated well so that all interfering influences were led down to the ground. The skin surface was moistened by distilled water to which—for the quinhydrone electrode—was added each time approximately half a teaspoonful of quinhydrone powder. As a measuring instrument* we employed a modern valve voltmeter of the Polymetron A. G. Zurich, to which both electrodes could be connected. Correction of temperature 24°C.

We took a total of about 2,000 comparative individual measurements on the extensor surface of the lower arm, on the flexor surface of the lower arm, on the palm of the hand, and on the back of the hand. For determining the pH-value in one of the 4 named skin areas we took on every patient 6 individual measurements each time on the lower arm and 4 on the hand, each time with the glass electrode. From this we deduced the average value and then took 6 resp. 4 individual measurements with the quinhydrone electrode in every area. The necessity of so many measurements is explained by the mosaic-type structure of the acid coat. Comparable average results can be obtained in only this way.

As we intentionally made the investigations on normal healthy, diseased, and freshly soaped skin, the following figures do not represent the average pH-values on normal healthy skin but they disperse towards the neutral point. With these measurements we were seeking for a comparison with which we thought a broad pH-spectrum was necessary.

* We are very much obliged to Herr Gauchat and Dr. Ingold of the Polymetron A. G., Zurich, for the kind support they gave us in this matter.

Thus we found with the glass electrode on the flexor surface of the lower arm with 40 patients an average of pH 5.03, whereas the quinhydrone electrode showed pH 4.99, which is a difference of -0.04 (against the glass electrode).

On the extensor surface of the lower arm the corresponding values were pH 5.12 with the glass electrode, pH 5.13 with the quinhydrone electrode, a difference of $+0.01$.

On the palm of the hand the glass electrode obtained in 40 patients an average of pH 5.39, the quinhydrone electrode one of 5.35, a difference of -0.04 .

The average of the measurements on the back of the hand with a glass electrode was pH 5.14, with the quinhydrone electrode pH 5.17, hence a difference of only $+0.03$.

These differences are very well within the range of the normal measuring deviation and it thus can be said that both electrodes completely correspond to one another, and so do the pH-values on the skin surface determined by the two electrodes.

Thus we have measuring electrodes that really suit the purpose of pH-determination on the skin surface—to which fact we referred in detail in “Hautarzt” (1952, 316) (6) with reference to quinhydrone electrodes.

This also may be said for the glass electrode with which the flat membrane is of highest importance as only thereby a steady, complete contact with the fluid film on the skin is made possible. With the help of sample tests we could prove that ball type glass electrodes were not efficient for skin measurements. Such a ball type electrode contacts the skin with but a small section of its surface, whereas in the preceding calibration the entire surface contacts the buffer solution and thus even air and fluid foreign portions cannot exercise any considerable influence on the measuring accuracy.

Also Arbenz' (1) investigations a year ago in this hospital are subject to this possibility of error as he took part of his measurements with a ball type glass electrode after the flat electrode he used in the beginning had broken and could not be replaced.

As Arbenz was working with a calibration solution of pH 7.0 his values for pH-determination on normal healthy skin—as our sample tests show—are likely to disperse towards the neutral point.

As our measurements with glass and quinhydrone electrodes show the same pH-values on the skin surface this proves the reliability of the measuring method with quinhydrone electrodes employed so far; and disproves the various objections to the effect that redox systems on the skin would essentially influence the measuring accuracy with quinhydrone electrodes.

(To appear in detail in the “Archiv für Dermatologie und Syphilis”).

REFERENCES

1. ARBENZ, H.: Untersuchungen über die pH-Werte der normalen Hautoberfläche. *Dermatologica*, **105**: 333, 1952.
2. BLANK, J. H.: Messung des pH der Hautoberfläche. *J. Invest. Dermat.*, **2**: 67, 1938.

3. INGOLD, W.: Elektroden für die Potentiometrie und ihre Anwendungen in Labor und Technik *Chimia* **5**: 196, 1951.
4. KLEFEHN, F.: Erprobung einer Glaselektrode zur Messung der Wasserstoffionenkonzentration der Hautoberfläche. Inaug. Diss. Freiburg, 1942.
5. KORDATZKI, W.: Taschenbuch für praktische pH-Messung, Müller u. Steinicke Verlag, 1948.
6. KORDATZKI, W. AND C. G. SCHIRREN: Vorläufige Mitteilung über eine neue Haut-pH-Messelektrode *Hautarzt*, 316, 1952.
7. KORDATZKI, W. AND C. G. SCHIRREN: Über eine neue Haut-pH-Messelektrode. *Klin. Wehnschr.*, 840, 1952.
8. KRATZ, L.: Die Glaselektrode und ihre Anwendung, Steinkopff-Verlag Frankfurt, 1950.
9. MARCHIONINI, A.: Physikalische, chemische Untersuchungen an der menschlichen Haut. *Klin. Wehnschr.*, 284, 1928.
10. MARCHIONINI, A.: Säuremantel der Haut und Bakterienabwehr. *Klin. Wehnschr.*, **663**: 773, 1938.
11. MARCHIONINI, A.: Untersuchungen über die Wasserstoffionenkonzentration der kranken Haut. *Arch. f. Dermat. u. Syph.*, **139**: 160, 1931.
12. MARCHIONINI, A.: Untersuchungen über die Wasserstoffionenkonzentration der Haut. *Arch. f. Dermat. u. Syph.*, **158**: 290, 1929.
13. SCHADE, H. AND MARCHIONINI, A.: Ueber die Acidose auf der normalen Haut und ihre Bedeutung zur Abwehr der Bakterien. *München. med. Wehnschr.*, **33**: 1435, 1927.
14. SCHADE, H. AND MARCHIONINI, A.: Der Säuremantel der Haut. *Klin. Wehnschr.*, 12, 1928.
15. SCHIRREN, C. G.: Vergleichende Haut-pH-Messungen. *Arch. f. Dermat. u. Syph.*, **197**: 73, 1953.